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The goal of this work was to develop computational procedures for the calculation of the nonlinear optical properties of molecules and to use these procedures to study the molecular nature of these effects. Of particular interest have been studies of the third-order effects. In the following sections, a short report will be given on the status of this work.

Methods

For an isolated molecule in a static, dc-electric field the energy may be written in terms of the field strength, F , as

$$E(F) = E(0) - \mu_i F_i - \frac{1}{2!} \alpha_{ij} F_i F_j - \frac{1}{3!} \beta_{ijk} F_i F_j F_k - \frac{1}{4!} \gamma_{ijkl} F_i F_j F_k F_l - \dots \quad (1)$$

In this expression α_{ij} are components of the molecular polarizability and β_{ijk} and γ_{ijkl} are components of the first and second hyperpolarizability, respectively. Summation over repeated indices is assumed. By truncation of equation 1 after the γ term, the molecular properties can be obtained by calculating the energy at several values of the applied field. This is the finite-field method as has been implemented in MOPAC 6.0 and GAMESS using the procedures presented in J. Comp. Chem.¹

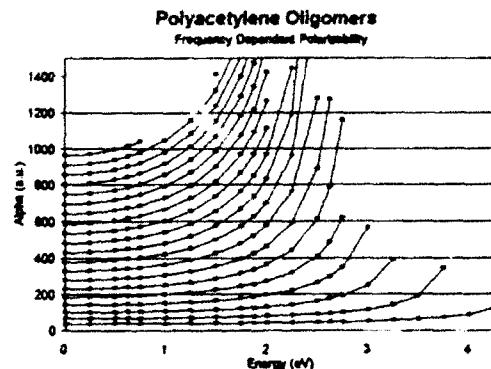
Two major problems with the finite-field method are it only provides static field values and it is subject to several numerical difficulties. Clearly to compare with experimental laser studies, the proper frequency dependent polarizability and hyperpolarizabilities are required. The method chosen to include these effects was the TDHF procedure of Bartlett and Sekino.² The procedure followed is very well described by Karna and Dupuis.³ This method all solves the numerical difficulties with the finite-

field procedure. The only disadvantage of the TDHF approach is that does not include electron correlation.

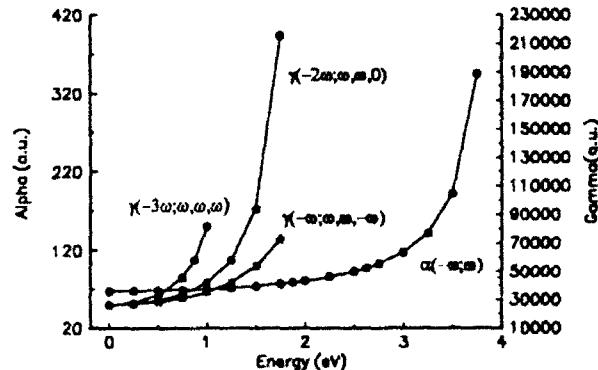
Oligomer calculations

a) polyacetylene:

The initial studies focused on using the finite-field procedures implemented in the MOPAC semiempirical program to treat very large systems such as oligomers and polymers. The first system examined was a series of polyene oligomers, $H(C_2H_2)_nH$, for n up to 20.⁴ The α and γ results compare very well with a series of *ab initio* calculations of Hurst, Dupuis, and Clementi.⁵ This system has recently been reexamined with the TDHF method to calculate the frequency dependent values as a test of the program and to explore the importance of these effects. The figure at the right shows the calculated values of $\alpha(-\omega; \omega)$.

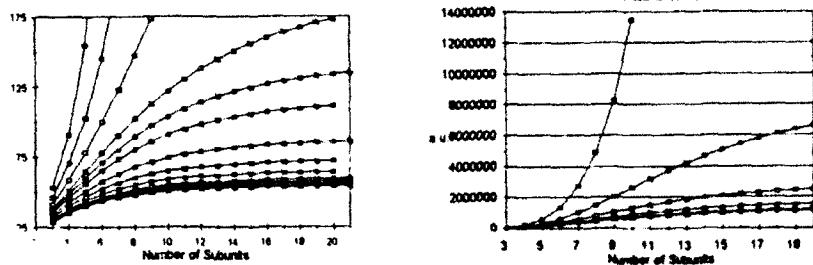


For γ , frequency dependence means there are several sets of data that can be obtained. We have calculated three different γ curves: $\gamma_{thg}(-3\omega; \omega, \omega, \omega)$, $\gamma_{efish}(-2\omega; \omega, \omega, 0)$, and $\gamma_{idir}(-\omega; \omega, \omega, -\omega)$ and the figure at the right shows a typical behavior of these quantities for $H(C_2H_2)_3H$.



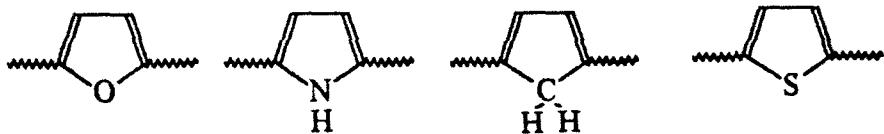
In this work we also studied the behavior of α and γ as the oligomer length is increased by adding subunits. Typical behaviors are shown below for $\alpha(-\omega; \omega)$ and $\gamma(-2\omega, \omega, \omega, 0)$. For the static quantities, α /subunit seems to saturate quite quickly, by around 12-14 units, while γ /subunit saturates at much longer oligomers, about 20 units. As the

frequency increases, the values/subunit still seem to saturate but at a higher value and at longer oligomers. However, if the frequency is increased even further, the quantities start to diverge (i.e., no saturation behavior). The energy at which this seems to happen is related to the excitation energy of the polymer (a little over 2 eV for polyacetylene).



b) Cyclopentadienes

In addition to the polyene oligomers, the heteroatom substituted polycyclopentadiene molecules shown below were studied.



These systems behave similarly to the polyene oligomers except they saturate the per subunit values at much smaller numbers of subunits. These systems were originally studied using the finite-field and are currently being reexamined using the TDHF procedure.

Hyperpolarizability Relationships

General formulas for third-order nonlinear optical processes have been developed.⁶ One such useful formula is

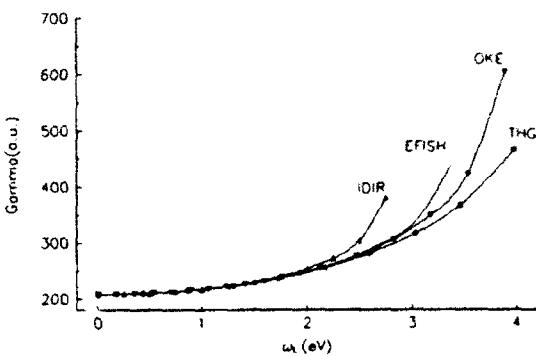
$$\gamma = \gamma^0 (1 + A \omega_L^2 + \dots), \quad (2)$$

where A is a frequency independent constant and the frequency parameter is given by $\omega_L^2 = \omega_\alpha^2 + \omega_1^2 + \omega_2^2 + \omega_3^2$. The importance of this type of equation is that if it can fit the data when truncated at the A term, it then allows the calculation of the dispersion in any type of γ from the knowledge of a fit on a single set of γ dispersion data. For example if A

is determined from a THG experiment (with $\omega_L^2 = 12\omega^2$), then equation 2 can be used to calculate the dispersion for either EFISH (with $\omega_L^2 = 6\omega^2$) or DFWM (with $\omega_L^2 = 4\omega^2$). When valid in the truncated form, this equation gives the simple relationship that the dispersion should be twice as great for THG as for EFISH and three times the amount in DFWM. If this type of expansion is valid then all second hyperpolarizabilities would be the same. Because of the pole behavior of γ , equation 2 can not be totally correct but it does work well for small frequencies, as shown to the right where the results for CH_2O are plotted versus ω_L . The utility of relationships between different types of hyperpolarizabilities demonstrates an important reason for adopting the convention where all γ values go to the same static limit.

Vibrational Corrections

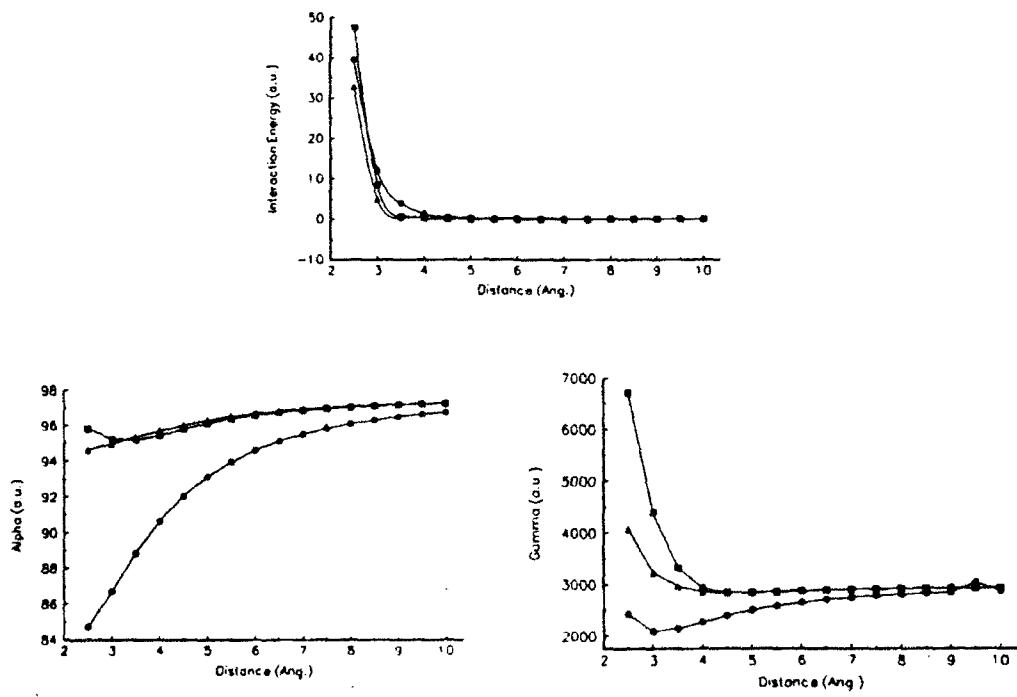
After the inclusion of frequency dependence, the next potentially large corrections to the calculations of hyperpolarizabilities are the inclusion of vibrational effects. A detailed method for calculating these effects has been worked out by Bishop and Kirtman⁷ and we have performed detailed SCF and MP2 calculations on water as a test molecule.⁸ From this work, the estimated vibrational correction for $\beta(0;0,0)$ is -37% of the electronic value and for $\gamma(0;0,0,0)$ is 15%. For the hyperpolarizabilities at higher frequency (0.0656 a.u.) the γ corrections are less [$\gamma(-\omega;\omega,0,0)$ 3%, $\gamma(-2\omega;\omega,\omega,0)$ -1%, $\gamma(-3\omega;\omega;\omega;\omega)$ ~0%, and $\gamma(-\omega,\omega,\omega,-\omega)$ 8%] but the corrections to β are significant [$\beta(-\omega;\omega,0)$ -19%, $\beta(-2\omega;\omega,\omega)$ 2%]. This same work shows however, that vibrational corrections have the potential to be enormous, 620% for $\beta(0;0,0)$ of NH_3 .



Intermolecular Effects

Another effect that may be important, particularly in condensed phase experiments, is intermolecular interactions. Initially, we have performed *ab initio* calculations on the approach of two ethylenes⁹ and have done a follow-up study for two acetylene molecules. The main results from these studies are that for *ab initio* calculations the choice of basis set is critical and very accurate results need to include correlation but reasonable results can be obtained at the RHF level.

Recently, we have been studying the approach of two benzene molecules. The initial calculations have been done at the AM1 level and show some interesting possibilities. The results are summarized for the interaction energy, alpha, and gamma for the face-to-face (circles), side-on (squares), and point-on (diamonds) approach of two molecules. At each distance, all other geometrical parameters were optimized.



The above results show very little effect on α for all but the face-to-face approach while for γ the effects are much larger, especially the side-to-side approach where the

increase in γ is about 150%. The energy requirements for approaching to 2.5 Å are no more than about 40-50 kcal.

Other Studies

Using the GAMESS based finite-field procedure, we began a study of systems where electron correlation effects are very important. Initial calculations were performed on the Be atom because the near degeneracy between the $1s^22s^2$ and $1s^22p^2$ levels makes normal perturbation treatments ill-behaved. The results are quite good and are summarized in a paper in *Chem. Phys. Lett.*¹⁰

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Below is a list of all the personnel at Memphis State University who have participated in the research supported by this grant.

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Clayton Spencer	Undergraduate Student (from Rhodes College, a nearby liberal arts college)
Shari Jones	A high school senior (funded by a university sponsored NIH program)